TABLE II

Product	n_D^{20}	d_4^{20}	r_D^{20}	I.V.	Sap V	n_{20} poises	Technical m.p.*	% total product
Reaction product 3a	1.4782	0.9223	0.3070	165	203	0.99	......	......
Solid fraction	1.4720	0.9147**	0.3061	91	212	......	27.0	28
Liquid fraction	1.4808	0.9255	0.3074	182	200	1.00	......	72

* Compare C. v. Vlodrop, Thesis Delft 1938, p. 109. ** Calculated from the d_4^{20} of the reaction product and the liquid fraction, using the ratios of the amounts of solid and liquid fractions.

at the same time the specific refraction sharply decreases. The acid values show that some saponification takes place, notably in the experiments at temperatures higher than 150°C.

Summary

A Norwegian cod liver oil upon treatment with sulphur dioxide under pressure shows cis-trans isomerization, conjugation (activation), and polymerization dependent on the reaction temperature. After a cis-trans isomerization the reaction product can be separated into a higher melting part with a decreased iodine value and a liquid part with an increased degree of unsaturation.

REFERENCES

1. H. I. Waterman, C. v. Vlodrop, J. Hannewijk, Verfkroniek *13*, 180 (1940). Research, Vol. I, 183 (1948); B. P. 502,390 (1939). H. I. Waterman, C. v. Vlodrop, W. J. Taat, Chimie et Industrie *44*, 285 (1940). E. A. M. F. Dahmen, Thesis Delft 1946.
2. H. I. Waterman, C. v. Vlodrop, M. J. Pfauth, Verfkroniek *13*, 130 (1940). Research, Vol. I, 186 (1948); B. P. 544,482 (1942).
3. H. I. Waterman and C. v. Vlodrop, J. Soc. Chem. Ind. *55*, 333T (1936); B. P. 480,677 (1938); U. S. P. 2,188,273 (1940).
4. H. I. Waterman, B. Pennekamp, D. P. A. Hak. Paper will appear in due course.
5. L. v. d. Hulst, Thesis Delft (1934); Rec. trav. chim. *54*, 639 (1935).

The Effect of Baking Powder Residues on Rancidity

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RESEARCH on the control of oxidative deterioration in the fat of bakery products has been reviewed by Triebold (13) and later by Lundberg (7). Several of the best known primary antioxidants, which are very effective in stabilizing edible oils and shortenings, do not protect the baked products made from these fats, either because the antioxidants are destroyed during the baking or because they become relatively more soluble in the aqueous than in the fat phase at the high pH of many baked products (8). This is true of the naturally occurring tocopherols and of propyl gallate. On the other hand, the antioxidant activity of nordihydroguaiaretic acid (NDGA), gum guaiac, and higher fatty acid esters of gallic acid (11) have been reported to carry over at least to some extent in baked products.

A number of compounds are known which enhance the effectiveness of primary antioxidants in fats. Various di- and polybasic inorganic and organic acids are the best known of such synergists, but many other compounds may show synergistic activity if coupled with a suitable primary inhibitor (10). Practically no work has been reported on the effectiveness of these synergists in baked products. In fact, very little information is at present available concerning their activity in any complex food containing an aqueous phase.

In the course of an investigation of frozen batter and dough products off odors and flavors were noted after varying periods of freezing storage which seemed to be associated with the type of baking powder employed. No tests were run at the time to determine whether the off odors were caused by oxidative deterioration of the fat. However since baking powders contain ingredients which are known to exert an antioxidant effect on dry fats containing primary inhibitors, it seemed worthwhile to investigate their effect on rancidity in a system more characteristic of baked products, i.e., where the fat is in contact with aqueous solutions usually having an alkaline reaction.

Commercially available baking powders belong to one of the following types, depending upon the nature of the acid ingredient (1):

1. Tartrate (cream of tartar and tartaric acid).
2. Calcium acid phosphate.
3. Combination (sodium aluminum sulfate and calcium acid phosphate).
4. Sodium acid pyrophosphate.

The residues from the heated powders consist of the salts of these acids.

Kaufman (4) mentions a catalytic effect of baking powders containing sodium aluminum sulfate on rancidity in products like prepared flour mixes. There is considerable evidence that aluminum itself has no effect on rancidity (2). Sulfuric, tartaric, and phosphoric acids all act as synergistic antioxidants, but there seems to be no published information of the effect of their anions on rancidity in alkaline solutions. The effectiveness of pyrophosphates in neutral as well as acid solutions was pointed out by Lea (6).

Experiments on Artificial Aqueous Fat Systems

Method. Rate of rancidification was followed in several experiments in which heated solutions of the four commercial types of baking powders were brought in contact with several different fats. Four grams of each powder were added to 100 ml. of water (a concentration within the range normally used in baking). Since it was desired to investigate the end products of baking powder reactions, the solutions were heated in a boiling water bath for a period of 20 minutes.

The pH of each solution was measured with a glass electrode. The pH for the same baking powder solution tended to increase with increased heating and with time elapsing after heating. The values recorded were those obtained at the beginning of an experiment; it is probable that a further shift took place during the course of the experiment.

The method used for obtaining contact between the fat and the aqueous solutions has been discussed in detail elsewhere (12). A 9-cm. filter paper (S & S No. 589, Black Ribbon) placed in a Petri dish absorbed 1.7 ml. of the heated baking powder solution to be tested. Melted fat (1.5 grams) containing .01% added carotene was weighed into a second filter paper and allowed to spread over the entire paper. This paper was then placed on top of the first. (Cutting the top paper slightly smaller than the bottom one eliminated any danger of lack of contact with the synergist at overlapping edges.) The fat penetrated rapidly throughout both papers, giving an even yellow color. A few drops of ethylene chloride were added to each dish as a preservative. The dishes were covered and placed on a rack in a tightly covered container with water in the bottom. Under these conditions moisture loss from the dishes was negligible if the experiments were terminated within a few days. However in the more stable combinations requiring a week or more to become rancid the dishes were completely sealed with paraffin to prevent evaporation of water and preservative. The experiments were conducted in an air oven at 40° or 50°C.

TABLE I

Effect of Heated Baking Powder Solutions on Rancidity in Lard

Type and brand of baking powder	Lard Sample 1		Lard Sample 2	
	pH	Hours to turn rancid 40°C.	pH	Hours to turn rancid 40°C.
Water control	5.8	124	5.8	43
Combination (Calumet)	8.3	76	7.8	12
Combination (KC)	8.1	90	....	....
Combination (Davis)	7.6	110	....	....
Tartrate (Royal)	7.5	76	7.0	20
Monocalcium phosphate (Rumford)	7.3	172	7.2	26
Pyrophosphate (Fleischmans)	8.0	315	7.8	360

Bleaching of the carotene served as a visible indication of the early stages of rancidity. The fat was extracted with carbon tetrachloride and peroxide determinations made at intervals after bleaching had progressed but before it was complete. Peroxide values were expressed as millimoles peroxide per 1,000 grams of fat. A peroxide value of 20 was accepted as the end of the induction period or beginning of rancidity.

Effect of Baking Powder Residues on Rancidity in Lard. Table I shows the effect of heated solutions of a number of commercial baking powders on rancidity in two samples of lard. In the less stable lard (Sample 2) all baking powders with the exception of the pyrophosphate accelerated rancidity as compared to the water control. In the more stable Sample 1 the monocalcium phosphate also gave some protection as compared to the water control. The pyrophosphate in both cases had an antioxidant effect far superior to that of any other powder.

The accelerating effect of the combination and tartrate powders is probably due to the high pH rather than to any specific prooxidant effect of the ingredients. Borate buffers within the pH range of these samples accelerated rancidity in plain lard to approximately the same extent as these baking powder solutions.

Effect of Copper. Lea has suggested that part, at least, of the antioxidant activity of pyrophosphates might be due to their ability to bind traces of copper and other metals. In order to determine whether the extreme differences noted between the combination and pyrophosphate powders might be due to the greater effectiveness of the pyrophosphate as a metal scavenger, 1 part per million of copper in the form of copper sulfate was added to solutions of each of the baking powders before heating and the effect of the copper solutions on rancidity in lard compared with controls containing no copper. The results (Table II)

TABLE II

Copper Binding Effect on Baking Powder Residues

Solution tested	Hours to turn rancid 40°C.
Borate buffer, pH 7.8	40
Buffer + 1 p.p.m. Cu	12
Combination (Calumet)	28
Calumet + 1 p.p.m. Cu	26
Pyrophosphate (Fleischmans)	195
Fleischmans + 1 p.p.m. Cu	120

show the combination powder to have a greater copper binding effect than the pyrophosphate. While both powders reduce the catalytic effect of small amounts of copper, the greater protection obtained with pyrophosphate as compared to combination powders is apparently due to the greater activity of the pyrophosphate as a synergistic antioxidant rather than to greater copper binding ability.

Lard With Added Phenolic Antioxidants. Results of a typical experiment comparing the effects of a combination and pyrophosphate powder on rancidity in lard containing added phenolic antioxidants are shown in Table III. This sample of lard was somewhat more stable than those previously used; the temperature of the oven was increased to 50°C. to cut down on time required for rancidity. Nordihydroguaiaretic acid (NDGA)[1] at a concentration of .005% was compared with alpha tocopherol at the same concentration and also with the same sample of lard containing only the small amount of tocopherol naturally present. While NDGA was a more effective stabilizer than the tocopherol in the control samples containing only water or buffer, in the presence of either of the baking powders added tocopherol was better than NDGA. Apparently these synergists are much more effective with alpha tocopherol than with NDGA. In fact, the protection obtained with the pyrophosphate and NDGA might be accounted for by the effect of the pyrophosphate on the tocopherol naturally present in the lard. On the other hand, marked synergisms between NDGA and phosphoric and citric acids in dry fats seem to be well established (5, 7, 9).

TABLE III

Effect of Baking Powder Solutions on Lard With Added Antioxidants

Solution tested	pH	Hours to turn rancid		
		Plain lard	Lard + .005% tocopherol	Lard + .005% NDGA
Water	5.8	100	220	300
Borate buffer	8.2	63	150	200
Combination (Calumet)	8.1	120	250	180
Pyrophosphate (Fleischmans)	7.8	300	750	450

In these experiments even the combination powder had a slight retarding effect on rancidity with plain

[1] Obtained through the courtesy of Nordigard Corp., Chicago, Ill.

lard as well as with lard plus added tocopherol. One experiment was performed with a hydrogenated vegetable oil which should contain naturally a much larger amount of tocopherol than that added to the lard. The experiment was faulty in that Petri dishes were unsealed and lost much moisture. Also the fat was not completely melted at the oven temperature of 40°C. It was terminated at the end of 68 days, at which time only the water control was rancid with a peroxide number of 88. The peroxide values of the fat in contact with the baking powder solutions were as follows: combination—27, tartrate—18, calcium acid phosphate—15, and pyrophosphate—8. It is evident that all types of baking powders have antioxidant activity in the presence of fats containing sufficient tocopherol. However the order of effectiveness remains the same, being least for a combination and greatest for a pyrophosphate powder. The observation that additional fat prevented rancidity in prepared flour mixes containing combination powders (4) is probably related to the synergistic action of the baking powder and possibly of other ingredients of the mix with the added tocopherol. Further work on baking powders with fats containing gum guaiac, lauryl gallate, other forms of tocopherol, etc., would be of interest in view of the differences obtained with NDGA and alpha tocopherol.

Experiments on Biscuits and Muffins

Method. Formulae used were as follows:

BISCUITS		MUFFINS	
Ingredients:		Ingredients	
Flour	244 g.	Flour	275 g.
Fat	60 g.	Fat	36 g.
Baking powder	8 g.	Baking powder	17 g.
Salt	6 g.	Salt	9 g.
Milk	188 ml.	Sugar	18 g.
		Egg	96 g.
		Water	354 ml.

Details of the mixing and baking procedures were standardized as far as possible. The pH of the baked products was determined by macerating one part with five parts of distilled water. The pH values were stable and showed no shift with time or further dilution. Because of the difficulty of preventing bacterial action during observation of oxidative changes in moist baked products not preserved by freezing, the accelerated tests were performed on dried crumbs. The biscuits and muffins were split and dried overnight at 50°F. They were then pulverized, the crumbs thoroughly mixed, and weighed out into Petri dishes in 10- or 20-g. portions. At appropriate intervals portions of the crumbs were extracted with carbon tetrachloride and peroxide determinations made on the filtered extract.

Some of the biscuits and muffins from each batch were packaged in cellophane containers and frozen at —17°C. for periods ranging from 60 to 90 days. At the end of the storage period they were thawed at room temperature and judged for odor and flavor by an adaptation of the paired eating method (3), i.e., products made with the same sample of fat but with two types of baking powder were compared, and the judges were asked to indicate the number of each pair having the better odor and flavor and the degree of difference between them by 1 to 4 plus marks. Peroxide numbers were also run on the extracted fat from each product at the end of the storage period.

Results. The results on accelerated rancidity tests (Table IV) demonstrate that biscuits and muffins made from the pyrophosphate powder were more resistant to rancidity than those from the combination powder. It is not of course possible with baked products to have a control containing no baking powder, but the two selected represent the commercial powders showing in the tests on artificial systems the least (combination) and the greatest (pyrophosphate) antioxidant effect. It is evident that the protective effect of the pyrophosphate is not confined to artificial systems, but carries over in baking.

TABLE IV
Effect of Baking Powder on Development of Rancidity in Biscuit and Muffin Crumbs

Product	Baking powder	Fat sample			
		Lard		Lard + .005% NDGA	
		pH	Days to turn rancid	pH	Days to turn rancid
Biscuits	Combination	6.8	14	6.8	17
	Pyrophosphate	7.1	38	7.1	28
Muffins	Combination	7.2	18	7.2	28
	Pyrophosphate	7.9	74	7.9	97

The higher pH of biscuits and muffins made with the pyrophosphate powder introduces a complicating factor which has not been adequately explored. In artificial systems an increase in pH results in more rapid rancidification, but there seem to be no published observations on effect of pH on rancidity in baked products. It is possible that a higher pH would promote the formation of reductones or other carbohydrate decomposition products which might have an antioxidant effect.

The lard to which NDGA was added (Table IV) was the same sample used for the plain lard experiments, but the products made with lard plus NDGA were made on a different day, with different batches of milk and eggs, thus the protective effect of the NDGA cannot be fairly appraised from these tests.

Biscuits and muffins made with hydrogenated vegetable oil (a very stable commercial shortening having a high melting point) were not rancid when the accelerated tests were terminated. Those made with the combination powder had the higher peroxide numbers, but the differences were not great. Muffins after 84 days of storage had peroxide numbers of 7 and 0 for combination and pyrophosphate powders respectively. Biscuits after 112 days of storage showed peroxide numbers of 17 and 11 for combination and pyrophosphate powders respectively.

Several experiments, in which lard biscuits made from the four different types of baking powders were prepared as described above but stored in aluminum moisture dishes rather than pyrex Petri dishes for the accelerated rancidity tests, showed a much faster rate of rancidification and less protective effect of the pyrophosphate. For example, in one such experiment, biscuits made with a combination powder turned rancid in 97 hours, tartrate 115, monocalcium phosphate 135, and pyrophosphate 145 hours. It was later discovered that the aluminum moisture dishes (probably an alloy of aluminum and copper) catalyzed oxidation of the fat as shown by the rapid appearance of a bleached ring at the area of contact when filter papers containing fat plus carotene were placed on the dishes. Pure aluminum foil had no such accelerating effect.

Of the frozen products those made with lard and combination powder had slight peroxide values (4 to 6) after the storage period whereas all others had no more than a trace. However, all eight judges rated lard and lard plus NDGA biscuits made with pyrophosphate powder better in odor than those made with combination powder, the difference between them being distinct (average 2 plus marks). The off odor in those made with the combination powder was described as "sharp" or "strong" rather than rancid and seemed qualitatively different from the distinctly rancid odor which developed during accelerated tests on the biscuit crumbs. It is possible that oxidation of some other constituent of the dough takes place during the early stages of fat peroxidation or that the decomposition of the peroxidized fat follows a different course in the moist frozen product. The odor scores on hydrogenated fat biscuits showed no significant difference for those made with combination versus pyrophosphate powder. With muffins all judges preferred the odor of the pyrophosphate products, whether the fat used was lard or hydrogenated vegetable oil.

Flavor scores, unlike the odor, were not significantly different for pyrophosphate powder versus combination powder products. It is probable that the "excess soda" taste associated with the greater alkalinity of products made with the pyrophosphate powder caused some of the judges to rate them down in flavor.

Summary and Conclusions. The effect on rancidity of heated residues of the four commercial types of baking powder was measured in artificial aqueous fat systems. The powders inhibited rancidity in such systems in the following order: combination, tartrate, monocalcium phosphate, and pyrophosphate—the combination being least effective and the pyrophosphate very much more effective than any other type.

The antioxidant effect of the pyrophosphate powder was shown to be due primarily to a synergism with tocopherol rather than to special ability of the pyrophosphate to bind traces of copper. The synergism was much more marked with tocopherol than with NDGA.

In accelerated tests on the dried crumbs, biscuits and muffins baked with a pyrophosphate powder had much greater resistance to rancidity than those made with a combination powder. When frozen, products made with the combination powder developed off odors more rapidly than those made with a pyrophosphate powder.

REFERENCES

1. Bailey, L. H., "Development and Use of Baking Powder and Baking Chemicals," U.S.D.A. Circ. 138 (1940).
2. Bryan, J. M., "Aluminum and Aluminum Alloys in the Food Industry," Food Invest. Spec. Rep. 50, Dept. Sci. and Indust. Research, London (1948).
3. Cover, S., Some Modifications of the Paired Eating Method in Meat Cookery Research, Food Research *5*, 237 (1942).
4. Kaufman, C. W., Common Ailments of Quality in Processed Foods, Food Indust. *18*, 80 (1946).
5. Kraybill, H. R., and Beadle, B. W., Oxidation Inhibitor for Fats and Oils, U. S. Patent 2,451,748 (1948).
6. Lea, C. H., "Rancidity in Edible Fats," Chem. Pub. Co., New York (1939).
7. Lundberg, W. O., "A Survey of Present Knowledge, Researches and Practices in the U. S. Concerning the Stabilization of Fats," Hormel Inst., U. of Minn. Pub. No. 20 (1947).
8. Mattil, K. F., and Black, H. C., A Laboratory Method for Determining the Ability of Antioxidants to Stabilize Fat in Baked Goods, J. Am. Oil Chem. Soc. *24*, 325 (1947).
9. Mattil, K. F., Filer, L. J., and Longenecker, H. E., A Study of the Antioxidant Effectiveness of Several Compounds on Vegetable Fats and Oils, Oil and Soap *21*, 160 (1944).
10. Mattill, H. A., Antioxidants, Ann. Rev. Biochem. *16*, 177 (1947).
11. Morris, S. G., Kraekel, L. A., Hammer, D., Myers, J. S., and Riemenschneider, R. W., Antioxidant Properties of the Fatty Alcohol Esters of Gallic Acid, J. Am. Oil Chem. Soc. *24*, 309 (1947).
12. Scarborough, D., and Watts, B. M., The Prooxidant Activity of Ascorbic Acid and Cysteine in Aqueous Fat Systems, Food Tech. *3*, 152 (1949).
13. Triebold, H. O., Oxidative Deterioration of Fats in Cereal Products, Oil and Soap *22*, 334 (1945).

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Comparative Study of the Oxidation and Polymerization of Linseed Oil by Application of Some Recently Developed Physical Techniques*

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RESEARCH and control of plant processing in the drying oil field have been in the past very much dependent on chemical analytical evaluation. Although the value of such work cannot be underestimated, there have been instances where the results of such analyses have not been reproducible nor applicable to a particular oil system. In recent years physical methods have found more and more application because of the accuracy and reproducibility of results as well as the simplicity of operating the various commercially available instruments.

It is the purpose of this paper to present three physical test methods which have been used in our laboratories for the study of polymerized and oxidized oils and which have found diverse application as research and plant processing control tools. These measurements are:

1. Molecular Weight.
2. Dielectric Constant.
3. Power Factor.

For the demonstration and investigation of these methods this study has been confined to experimental procedures performed with linseed oil although in the course of this and prior work a considerable amount of data was obtained for other vegetable and marine oils. Specifically, raw linseed oil was thermally polymerized and mechanically oxidized; samples were withdrawn from each batch at various intervals for analysis. The raw linseed oil used in these preparations had the following constants:

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